# Cycloadducts of Nitrones with Isocyanates; 1,2,4- or 1,3,4-Oxadiazolidinones?

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The adducts formed between various aryl-substituted nitrones and aryl isocyanates have been shown, using $^{15}N$ n.m.r. spectroscopy and *X*-ray crystallography, to be substituted 1,2,4-oxadiazolidinones and not the previously reported 1,3,4-oxadiazolidinones.



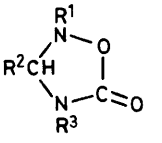
The formation of adducts of nitrones with isocyanates has been known for nearly a century, and in 1890 Beckmann [1] assigned the 1,2,4-oxadiazolidinone structure (**1a**) to the adduct of *N*-benzyl-*C*-phenylnitrone with phenyl isocyanate on the basis of its conversion into *N*-benzyl-*N'*-phenylbenzamidine by reaction with sodium methoxide. During an extensive study of 1,3-dipolar cycloadditions, Huisgen *et al.* reported other nitrone–isocyanate adducts and assigned the structure (**1b**) to the adduct of *N*-methyl-*C*-phenylnitrone with phenyl isocyanate.[2] The most significant evidence quoted for this structure was the low-resolution mass spectrum in which a fragment of *m/z* corresponding to the ion $PhC{=}N^{+}Ph$ was observed, with other ions attributable to phenyl isocyanate and the nitrone. The adduct of *C,N*-diphenylnitrone with phenyl isocyanate was also reported and assigned structure (**1c**) by analogy with compound (**1b**). This adduct was subsequently re-examined and structure (**1c**) was confirmed by alkaline hydrolysis to be *N,N*-diphenylbenzamidine.[3] Shortly before the publication of this result, a communication appeared in which the adducts of phenyl isocyanate with *N*-phenyl-*C*-(2-tolyl)nitrone and *N*-phenyl-*C*-(3-tolyl)nitrone were assigned the 1,3,4-oxadiazolidinone structures (**2d**) and (**2e**).[4] These structures, which were suggested to arise from the initially formed adducts (**1d**) and (**1e**) by a dissociation–recombination process, were assigned solely on the basis of the n.m.r. chemical shifts of the ring methine protons, which were considered to be at too high a frequency for the molecular environment in compound (**1**). The formation of a range of adducts of structure (**2**) from the cycloaddition of nitrones with isocyanates is claimed in a subsequent paper[5] in which the chemical shifts reported for the ring methine protons (δ 5.7—6.3) and carbon atoms (δ 110—119) are quoted as supporting evidence. If these adducts were of structure (**2**), this would have a similarity to some cases of cycloaddition reactions of the nitrones with ketenes,[3] but the evidence in favour of structure (**2**) seemed very tenuous. We have prepared a substantial number of nitrone–isocyanate adducts and investigated their structures by a variety of techniques. No evidence was found to support structure (**2**) and all the conclusive results point to structure (**1**) as being of the correct constitution. An early attempt to establish the structure of compounds (**1d**)/(**2d**) by alkaline hydrolysis to the amidine, as for compound (**1c**), was unsuccessful and chemical degradation was abandoned in favour of spectroscopic investigation.

Natural abundance $^{15}N$ n.m.r. spectroscopy was the most informative technique employed. All of the ten compounds which were examined had two $^{15}N$ signals in the ranges δ −193 to −199 and δ −267 to −276 (see Table 1), and the spiro adducts (**3a**) and (**3b**)[3] had signals at similar chemical shifts. The *N,N'*-diphenylhydrazine derivatives (**4a**) and (**4b**) were used as model compounds to give an indication of the $^{15}N$ chemical shifts expected for compounds of structure (**2**), and it is clear that the signal at *ca.* δ −195 is at approximately 50 p.p.m. too

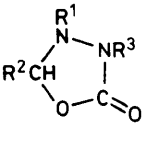
**Table 1.**

| Compd. | $\delta_H$ [a] | $\delta_C$ [b] | $\delta_N$ [c] | |
|---|---|---|---|---|
| (**1b**) | 5.59 | 85.1 | −199.1 | −268.5 |
| (**1c**) | 6.15 | 86.5 | −193.5 | −269.5 |
| (**1d**) | 6.40 | 83.2 | −193.3 | −269.9 |
| (**1f**) | 6.47 | 83.0 | | |
| (**1g**) | 5.92 | 87.6 | −193.2 | −270.2 |
| (**1h**) | 6.24 | 80.0 | | |
| (**1i**) | 6.13 | 88.1 | | |
| (**1j**) | 6.00 | 85.4 | −197.6 | −267.5 |
| (**1k**) | 5.73 | 87.1 | | |
| (**1l**) | 5.92 | 87.4 | | |
| (**1m**) | 5.43 | 87.4 | −197.7 | −268.7 |
| (**1n**) | 5.64 | 85.6 | −197.0 | −274.1 |
| (**1o**) | 5.64 | 88.0 | −196.5 | −270.6 |
| (**1p**) | 5.38/5.74 | 82.9/86.7 | −197.7 | −270.1 |
| (**1q**) | 5.99 | 82.4 | −196.6 | −276.3 |
| (**3a**) | | 92.0 | −192.3 | −264.9 |
| (**3b**) | | 92.7 | −185.1 | −265.4 |
| (**4a**) | | | −248.9 | −272.0 |
| (**4b**) | | | −270.8 [d] | −281.7 |

[a] Ring methine proton. [b] C-3 Of the heterocyclic ring. [c] With respect to $CH_3NO_2$, negative δ values correspond to resonance at lower frequency. [d] NH, *J* 87 Hz.



(**1**)

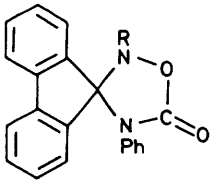


(**2**)

| | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| **a**; | $PhCH_2$ | Ph | Ph |
| **b**; | Me | Ph | Ph |
| **c**; | Ph | Ph | Ph |
| **d**; | Ph | 2-$MeC_6H_4$ | Ph |
| **e**; | Ph | 3-$MeC_6H_4$ | Ph |
| **f**; | Ph | 2-$MeC_6H_4$ | 2-$MeOC_6H_4$ |
| **g**; | Ph | Ph | 2-$MeC_6H_4$ |
| **h**; | Ph | 2-Furyl | Ph |
| **i**; | Ph | Ph | 1-Naphthyl |
| **j**; | 2-$MeC_6H_4$ | Ph | Ph |
| **k**; | 2-$MeC_6H_4$ | Ph | 2-$MeC_6H_4$ |
| **l**; | 2-$MeC_6H_4$ | Ph | 1-Naphthyl |
| **m**; | Me | Ph | 2-$MeC_6H_4$ |
| **n**; | Me | Ph | 2-$MeOC_6H_4$ |
| **o**; | Me | Ph | 1-Naphthyl |
| **p**; | Me | 2-$MeC_6H_4$ | 2-$MeC_6H_4$ |
| **q**; | Me | 2-$MeC_6H_4$ | 2-$MeOC_6H_4$ |

**Table 2.** Refined atomic co-ordinates for compound (**1m**)

| | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| O(1) | 0.556 6(2) | 0.293 0(1) | 0.080 0(1) |
| O(2) | 0.364 1(2) | 0.369 1(1) | 0.097 45(9) |
| N(1) | 0.423 4(2) | 0.340 7(1) | −0.023 0(1) |
| N(2) | 0.278 8(2) | 0.417 9(1) | 0.044 1(1) |
| C(1) | 0.459 3(3) | 0.330 1(1) | 0.052 4(1) |
| C(2) | 0.275 9(2) | 0.372 4(1) | −0.027 2(1) |
| C(3) | 0.133 6(3) | 0.424 4(2) | 0.078 7(2) |
| C(4) | 0.245 8(3) | 0.421 0(1) | −0.096 8(1) |
| C(5) | 0.326 2(3) | 0.486 4(2) | −0.111 0(2) |
| C(6) | 0.291 4(4) | 0.531 5(2) | −0.174 4(2) |
| C(7) | 0.178 8(4) | 0.510 7(2) | −0.223 6(2) |
| C(8) | 0.100 6(4) | 0.445 6(2) | −0.210 2(2) |
| C(9) | 0.133 8(3) | 0.400 6(2) | −0.146 5(2) |
| C(10) | 0.491 2(3) | 0.303 1(1) | −0.087 3(1) |
| C(11) | 0.634 3(3) | 0.319 6(1) | −0.106 2(2) |
| C(12) | 0.693 1(3) | 0.285 5(2) | −0.171 8(2) |
| C(13) | 0.611 2(3) | 0.237 4(1) | −0.218 0(2) |
| C(14) | 0.469 6(3) | 0.221 7(1) | −0.198 3(1) |
| C(15) | 0.409 2(3) | 0.254 1(1) | −0.132 4(1) |
| C(16) | 0.727 7(3) | 0.375 0(2) | −0.058 7(2) |




(3) **a**; Me
**b**; Ph


(4) **a**; $CO_2Et$
**b**; $CH_2Ph$

high a frequency for structure (**2**) but would be consistent with deshielding by an adjacent oxygen atom as in structure (**1**). An attempt to synthesize (**2c**) unambiguously by the reaction of compound (**4a**) with benzaldehyde under basic conditions was unsuccessful.

The $^{13}C$ chemical shift of the ring methine carbon atom has been cited as evidence for structure (**2**).[5] The figure quoted (δ ~115) seemed surprisingly high for an $sp^3$ hybridised carbon, and we have checked the assignment by a two-dimensional $^1H$ and $^{13}C$ correlation spectrum for (**1c**)/(**2c**). This shows clearly that the proton resonating at δ 6.15 is attached to the carbon atom absorbing at δ 86.5, with the signal at δ 117 correlating with a proton signal at δ 7. All of the adducts examined have a $^{13}C$ n.m.r. signal in the range δ 80—88, and adducts (**3a**) and (**3b**) have a signal at *ca.* δ 92[3] attributable to the spiro carbon atom. Although we were unable to measure the $^{15}N$ n.m.r. spectra for all of the adducts prepared, the consistency of the $^{13}C$ n.m.r. signals for the ring methine carbon atoms is strong evidence for a common ring structure for all of the compounds (**1**) or (**2**). It is expected that a change from compound (**1**) to compound (**2**) would produce a change in the chemical shift of this carbon atom of about 20 p.p.m., well outside the range observed. Given the chemical evidence already available in support of structure (**1c**)[3] and the mass spectrometric evidence for (**1b**),[2] the pattern of $^{15}N$ and $^{13}C$ chemical shifts strongly favours structure (**1**) for all these adducts. There is, however, quite a variation observed in the chemical shift of the ring methine proton, which, in the absence of other data, might be

**Table 3.** Bond lengths (Å) and bond angles (°) with estimated standard deviations in parentheses for compound (**1m**)

| | | | |
|---|---|---|---|
| **Bond lengths** | | | |
| O(1)–C(1) | 1.203(3) | C(6)–C(7) | 1.387(5) |
| C(1)–N(1) | 1.353(3) | C(7)–C(8) | 1.373(5) |
| C(1)–O(2) | 1.356(3) | C(8)–C(9) | 1.388(4) |
| N(1)–C(2) | 1.467(3) | C(9)–C(4) | 1.385(4) |
| N(1)–C(10) | 1.432(3) | C(10)–C(11) | 1.385(3) |
| C(2)–N(2) | 1.467(3) | C(11)–C(12) | 1.389(4) |
| C(2)–C(4) | 1.498(3) | C(11)–C(16) | 1.535(4) |
| N(2)–O(2) | 1.481(3) | C(12)–C(13) | 1.384(4) |
| N(2)–C(3) | 1.464(3) | C(13)–C(14) | 1.372(4) |
| C(4)–C(5) | 1.390(4) | C(14)–C(15) | 1.386(3) |
| C(5)–C(6) | 1.387(4) | C(15)–C(10) | 1.384(3) |
| **Bond angles** | | | |
| O(1)–C(1)–N(1) | 129.4(2) | C(9)–C(4)–C(5) | 120.1(2) |
| O(1)–C(1)–O(2) | 121.9(2) | C(4)–C(5)–C(6) | 119.4(3) |
| O(2)–C(1)–N(1) | 108.8(2) | C(5)–C(6)–C(7) | 120.2(3) |
| C(1)–N(1)–C(10) | 124.9(2) | C(6)–C(7)–C(8) | 120.5(3) |
| C(1)–N(1)–C(2) | 109.0(2) | C(7)–C(8)–C(9) | 119.7(3) |
| C(10)–N(1)–C(2) | 122.6(2) | C(8)–C(9)–C(4) | 120.2(3) |
| N(1)–C(2)–N(2) | 98.6(2) | N(1)–C(10)–C(11) | 119.8(2) |
| N(1)–C(2)–C(4) | 115.4(2) | N(1)–C(10)–C(15) | 119.1(2) |
| C(4)–C(2)–N(2) | 111.2(2) | C(15)–C(10)–C(11) | 121.0(2) |
| C(2)–N(2)–O(2) | 102.3(2) | C(10)–C(11)–C(12) | 118.0(2) |
| C(2)–N(2)–C(3) | 111.5(2) | C(10)–C(11)–C(16) | 122.5(2) |
| C(3)–N(2)–O(2) | 105.9(2) | C(16)–C(11)–C(12) | 119.5(2) |
| N(2)–O(2)–C(1) | 106.3(2) | C(11)–C(12)–C(13) | 121.4(3) |
| C(2)–C(4)–C(5) | 121.1(2) | C(12)–C(13)–C(14) | 119.7(2) |
| C(2)–C(4)–C(9) | 118.9(2) | C(13)–C(14)–C(15) | 120.0(2) |
| | | C(14)–C(15)–C(10) | 119.9(2) |

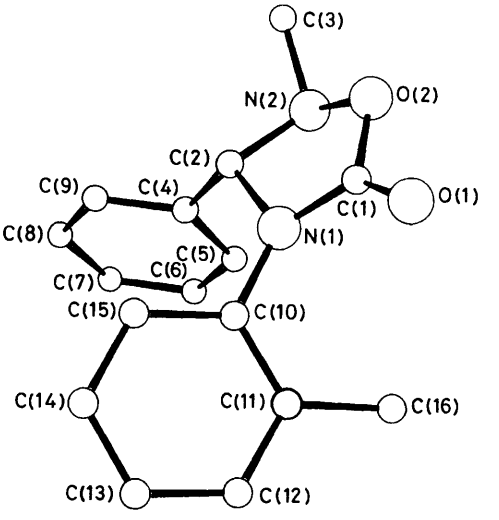



**Figure.** Molecular structure of compound (**1m**)

taken to indicate an alternation between structures (**1**) and (**2**) in the compounds studied.

Attempts were also made to use nuclear Overhauser difference measurements to determine the relative spatial positions of the groups $R^1$, $R^2$, and $R^3$ and the ring methine proton. Only in the case of (**1m**)/(**2m**) was this successful. In this case irradiation of the methine signal at δ 5.43 produced enhancement of the *N*–Me (3%) and the Ar–Me (1%) signals, whilst irradiation of the *N*–Me and Ar–Me signals produced enhancement of the methine signal in both cases (12% and 5%,

**Table 4.** Selected torsion angles (°) for compound (**1m**)

| | | | |
|---|---|---|---|
| C(1)–N(1)–C(2)–N(2) | 33.2 | C(2)–N(1)–C(10)–C(15) | −41.3 |
| N(1)–C(2)–N(2)–O(2) | −37.0 | C(1)–N(1)–C(2)–C(4) | 151.7 |
| C(2)–N(2)–O(2)–C(1) | 31.0 | N(1)–C(2)–C(4)–C(9) | 121.2 |
| N(2)–O(2)–C(1)–N(1) | −10.3 | N(2)–C(2)–C(4)–C(5) | 51.2 |
| O(2)–C(1)–N(1)–C(2) | −15.0 | N(1)–C(2)–C(4)–C(5) | −60.1 |
| C(10)–N(1)–C(1)–O(1) | 5.4 | N(2)–C(2)–C(4)–C(9) | −127.6 |
| C(10)–N(1)–C(1)–O(2) | −174.2 | C(3)–N(2)–C(2)–N(1) | −149.8 |
| C(10)–N(1)–C(2)–N(2) | −166.9 | C(3)–N(2)–C(2)–C(4) | 88.6 |
| C(10)–N(1)–C(2)–C(4) | −48.5 | O(2)–N(2)–C(2)–C(4) | −158.6 |
| C(1)–N(1)–C(10)–C(11) | −68.5 | C(1)–O(2)–N(2)–C(3) | 147.9 |
| C(1)–N(1)–C(10)–C(15) | 115.3 | N(2)–O(2)–C(1)–O(1) | 170.1 |
| C(2)–N(1)–C(10)–C(11) | 134.9 | C(2)–N(1)–C(1)–O(1) | 164.7 |



respectively). No sign of *N*–Me–Ar–Me interaction was evident, and these results point to compound (**1m**) as the correct structure. Similar experiments with structures (**1p**) and (**1q**) were inconclusive. In the case of compound (**1p**), irradiation of the ring methine proton enhanced the *N*–Me signal and one of the *C*–Me signals, but it was impossible to excite the *C*–Me group independently. Excitation of the *N*–Me group gave no enhancement of *C*–Me signals. Likewise with compound (**1q**) no interaction between *O*–Me protons and ring methine or *N*–Me protons could be detected.

The structure of compound (**1m**) was finally confirmed by an *X*-ray crystallographic study. The structure was solved using the direct methods MULTAN-80[6] programme and refined with the CRYSTALS[7] package. In a late state of the refinement, all the hydrogen atoms were located from a Fourier difference map and, with the exception of the *N*–Me group, were included in their calculated positions. The *N*–Me group was disordered and no attempt was made to refine this disorder, and these hydrogen atoms ($6 \times \frac{1}{2}$ atoms) were included in their found positions. None of the hydrogen atoms were refined, the final *R* value attained was 0.0424 ($R_w = 0.049$).

The structures of a number of unsaturated 1,2,4-oxadiazoles have been determined previously[8] but compound (**1m**) appears to be the first example of saturated 1,2,4-oxadiazolidin-5-one recorded. The final atomic co-ordinates are contained in Table 2 while bond lengths and angles are shown in Table 3. The Figure illustrates the molecular structure. Relevant torsion angles associated with the heterocyclic ring are contained in Table 4, and these indicate this ring adopts an approximate half-chair conformation with the three substituents equatorial. Equations to planes have been calculated for the five atoms of the heterocyclic ring and for the two aryl residues. Details of these together with refined thermal parameters are available on request from the Cambridge Crystallographic Data Centre.*

It was noticeable that in the n.m.r. spectra of all of the adducts in which $R^1$ = Me, there was a broadening of the $^1H$ and $^{13}C$ signals due to the *N*–Me group and ring methine group, presumably due to a slow inversion about the methyl-substituted nitrogen atom. In the case of compound (**1p**), both the proton signals were split into two distinct peaks, and during the n.O.e. experiment it was observed that excitation of the *N*–Me group resulted in enhancement of both the methine proton absorptions. These observations may be taken as additional evidence for structures (**1**) rather than (**2**) since inversion at nitrogen in compound (**2**) would be a much more rapid process.[9],†

* See Instructions for Authors (1987), *J. Chem. Soc., Perkin Trans. 1*, 1987, Issue 1.

† We thank a referee for pointing out the likely difference in inversion barriers in structures (**1**) and (**2**).

**Table 5.**

| Compd. | M.p. (°C) [from solvent][a] | Molecular formula | Analyses [Found (Calc.)] (%) C | H | N |
|---|---|---|---|---|---|
| (**1f**) | 130 [A + B] | $C_{22}H_{20}N_2O_3$ | 72.9 (73.3) | 5.7 (5.6) | 7.5 (7.8) |
| (**1g**) | 115 [A + B] | $C_{21}H_{18}N_2O_2$ | 76.4 (76.4) | 5.7 (5.5) | 8.6 (8.5) |
| (**1i**) | 140 [C + D] | $C_{24}H_{18}N_2O_2$ | 78.3 (78.7) | 5.0 (4.9) | 7.7 (7.7) |
| (**1j**) | 153 (decomp.) [C] | $C_{21}H_{18}N_2O_2$ | 76.4 (76.4) | 5.6 (5.5) | 8.5 (8.5) |
| (**1k**) | 128—130 (decomp.) [C + D or E] | $C_{22}H_{20}N_2O_2$ | 76.5 (76.7) | 5.7 (5.8) | 8.5 (8.1) |
| (**1l**) | 143—145 (decomp.) [C] | $C_{25}H_{20}N_2O_2$ | 79.1 (79.0) | 5.2 (5.2) | 7.4 (7.4) |
| (**1m**) | 152—154 [B] | $C_{16}H_{16}N_2O_2$ | 71.4 (71.6) | 6.0 (6.0) | 10.6 (10.5) |
| (**1n**) | 91—93 [B] | $C_{16}H_{16}N_2O_3$ | 67.7 (67.6) | 5.8 (5.6) | 10.2 (9.9) |
| (**1o**) | 150—152 [B + E] | $C_{19}H_{16}N_2O_2$ | 74.8 (75.0) | 5.3 (5.3) | 9.0 (9.2) |
| (**1p**) | 69—71 [B] | $C_{17}H_{18}N_2O_2$ | 72.3 (72.3) | 6.7 (6.4) | 10.1 (9.9) |
| (**1q**) | 164 [C + F] | $C_{17}H_{18}N_2O_3$ | 68.2 (68.5) | 6.2 (6.0) | 9.5 (9.4) |

[a] Solvents: A, water; B, methanol; C, ethyl acetate; D, light petroleum (b.p. 60—80 °C); E, acetone; F, ethanol.

A number of the adducts prepared, such as compound (**1i**) decomposed to dark tars slowly on storage at room temperature, and it was noticeable that adducts [(**1j**), (**1k**), and (**1l**)] decomposed at their m.p.s with gas evolution, unlike all the others. G.l.c. analysis of the dark oil produced by thermal decomposition of compound (**1j**) showed seven significant components. The four of lowest b.p. were identified by g.l.c.–mass spectrometry and g.l.c. peak enhancement as aniline, *o*-toluidine, benzylideneaniline, and benzylidene-*o*-toluidine. The components of higher b.p. were not identified. The formation of benzylideneaniline is consistent with structure (**1j**) rather than (**2j**). We suggest that the thermal instability of these three compounds is due to the steric effect of the methyl group on the 2-tolyl substituent which will keep this aromatic ring approximately perpendicular to the plane of the heterocyclic ring. In this conformation, conjugation will assist the homolysis of the adjacent N–O bond leading, after loss of $CO_2$, to the diradical $R^1\dot{N}CHR^2\dot{N}R_3$ and thence the observed products.

In conclusion, although the possibility of the formation of the adducts of structure (**2**) from the reaction of nitrones with isocyanates cannot be excluded, there appears to be no good evidence for thinking that any adducts so far reported, in this paper or elswhere, have structures differing from compound (**1**).

## Experimental

$^1H$, $^{13}C$, and $^{15}N$ N.m.r. spectra were measured with a Bruker AM250 spectrometer for solutions in deuteriochloroform. $^{15}N$ N.m.r. spectra were recorded at 25.35 MHz in 10 mm diameter n.m.r. tubes. Samples were dissolved in deuteriochloroform containing 0.1M nitromethane and 0.1M $Cr(acac)_3$ relaxation reagent, and varied in concentration between 0.1 and 0.4M depending on solubility. Spectra were run proton-decoupled

with suppression of n.O.e. using a 30° pulse angle, an acquisition time of 1 s, and a relaxation delay time of 3 s. The total data acquisition time varied from 14 to 50 h.

All the adducts reported were prepared by reaction of stoicheiometric proportions of the nitrone and isocyanate in dichloromethane at room temperature for 24 h. Analytical data *etc.* for new compounds are recorded in Table 5.

N-(2-*Methylbenzylidene*)*methylamine* N-*Oxide*.—A solution of *N*-methylhydroxylamine hydrochloride (5 g), sodium acetate (6 g, anhydrous), acetic acid (3 ml), and *o*-tolualdehyde (6.8 ml) in ethanol (10 ml) and water (15 ml) was left at room temperature for 36 h. The mixture was evaporated to dryness, and the residue extracted with chloroform. The chloroform solution was washed with aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and evaporated to leave the nitrone as a hygroscopic oil, which was not further purified but used in this crude form for the preparation of adducts (**1p**) and (**1q**).

*Crystal Data for Compound* (**1m**).—$C_{16}H_{16}N_2O_2$, $M$ = 268.315, $a$ = 9.180 4(6), $b$ = 17.615 6(10), $c$ = 17.222 7(19), $U$ = 2 785.21 Å$^3$, space group *Pbca*, $D_c$ = 1.28 g cm$^{-3}$, $Z$ = 8, Cu-$K_\alpha$ radiation ($\lambda$ = 1.5418 Å), $\theta \leqslant 66°$, 2 428 reflections scanned and of these 1 423 had $I \geqslant 3\sigma(I)$ and were used in the refinement $R$ = 0.0424, $R_w$ = 0.049. Crystal size 0.4 × 0.25 × 0.2 mm.

## References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*Received* 23*rd October* 1986; *Paper* 6/2066